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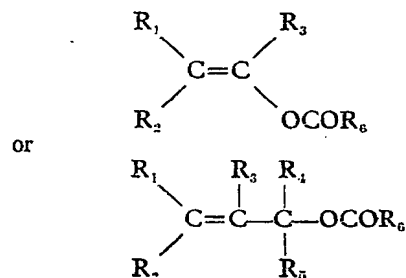


(54) PROCESS FOR THE PRODUCTION OF OLEFINIC COMPOUNDS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THE PRESENT INVENTION relates to the production of olefinic compounds.

According to the invention a vinyl or allyl ester of formula



respectively in which R_1 , R_2 , R_3 , R_4 , R_5 are hydrogen, an organic substituent or a halogen atom and R_6 is an alkyl group with a straight or branched carbon atom chain, a substituted alkyl group, a phenyl or substituted phenyl group or hydrogen, is contacted with a nucleophilic reagent of formula HA in which H is hydrogen and A a nucleophilic element or group in the presence of a Group VIII metal and a salt of copper, iron, cobalt, nickel, tin or lead.

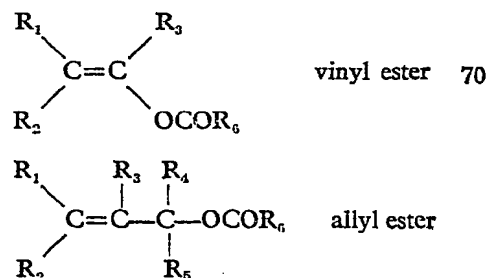
The Group VIII metals are iron, cobalt, nickel, platinum, palladium, iridium, rhodium, ruthenium and osmium. Preferably the Group VIII metal is a Group VIII noble metal, especially palladium. The metal may be introduced to the reaction as a fine powder or may be formed in situ by precipitation from solution. Thus palladous chloride may be added in solution from which metallic palladium may be precipitated by reductive side reactions.

[Price 5s. 0d. (25p)]

This precipitation takes place over a period of time and initially the reaction rate is slow, increasing as the metallic palladium is precipitated. It is advantageous to agitate the reaction solution to maintain the Group VIII metal in suspension. This may be achieved in a variety of ways, for example, by stirring. The amount of Group VIII metal used is preferably at least 0.00001 gram atoms per litre of solution, more preferably 0.001 to 0.1 gram atoms per litre of solution. When a salt of iron, cobalt or nickel is used it is possible to employ them in conjunction with metallic iron, cobalt or nickel respectively as the representative of the Group VIII metal.

The salt of copper, iron, cobalt, nickel, tin or lead may be a halide, e.g. copper chloride or ferrous bromide, or a carboxylate, e.g. copper acetate. Other salts such as a nitrate or a sulphate may also be used. The concentration of the copper, iron, cobalt, nickel, tin or lead salt is preferably at least 0.005 mole/litre, more preferably in the range 0.01 to 2.0 mole/litre. Two or more of these salts of the same or different metals may be used. It is particularly preferred to have the molar concentration of the salt of copper, iron, cobalt, nickel, tin or lead at least six times the molar concentration of the Group VIII metal.

The vinyl or allyl esters which are used in the process of the present invention are represented by the formulae:



INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

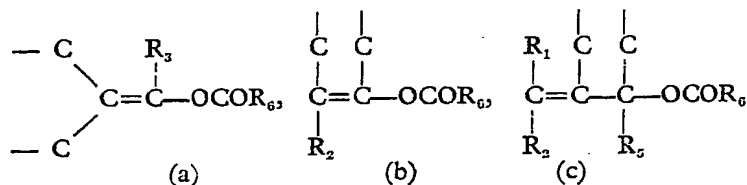
PCT/US 95/16631

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4740330	26-04-88	NONE	
US-A-4507492	26-03-85	NONE	
EP-A-0370946	30-05-90	JP-A- 2180877	13-07-90

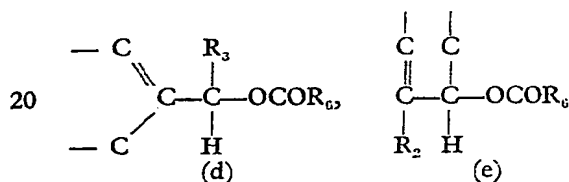
in which R_1 , R_2 , R_3 , R_4 and R_5 may be hydrogen, an organic substituent or a halogen atom, and R_6 is an alkyl group with a straight or branched carbon atom chain, a substituted alkyl group, a phenyl or substituted phenyl group, or hydrogen.

The organic substituents represented by R_1 , R_2 , R_3 , R_4 and R_5 may be alkyl, cyclo-

alkyl, aryl or heterocyclic groups, or any two of the groups R_1 , R_2 , R_3 , R_4 and R_5 on the same or adjacent carbon atoms may be combined in such a way that the carbon atom or atoms concerned are included in a cycloalkyl, aryl or heterocyclic ring. In this case structures of the type (a), (b) and (c) are obtained.



The vinyl esters (a) and (b) however may be unstable and isomerise to give the corresponding allyl structures (d) and (e).



which also may be used in the process of the invention. Preferred esters are those of the lower aliphatic carboxylic acids, particularly acids containing up to 6 carbon atoms for example acetic and propionic acids. Thus vinyl acetate, isopropenyl acetate, allyl acetate and methallyl acetate may be used in the process of the present invention.

The nucleophilic reagents in the process of the invention are of the formula HA in which H is hydrogen and A a nucleophilic element or group. Suitable nucleophilic reagents are primary or secondary amines, diamines, polyamines, phenols, mercaptans, thiophenols, amides, hydrogen cyanide and preferably, acids, alcohols or water.

The acids may be organic or inorganic acids. Thus the mineral acids, particularly the halogen hydric acids, may be used, for example hydrochloric or hydrobromic acid. Organic acids which may be reactants in the process include aliphatic mono- and di-carboxylic acids containing 1 to 20 carbon atoms e.g. lauric and stearic acids and adipic acid, aromatic mono-carboxylic acids e.g. benzoic acid, and aromatic di-carboxylic acids e.g. ortho-, iso- and tere-phthalic acids. When the

nucleophilic reagent is an acid, esters are obtained, e.g.:

allyl acetate with hydrogen chloride gives allyl chloride

vinyl acetate with hydrogen bromide gives vinyl bromide

allyl acetate with terephthalic acid gives diallyl phthalate

methallyl acetate with benzoic acid gives methallyl benzoate.

Monohydric, dihydric and polyhydric alcohols may be used as the nucleophilic reagents in the process. Preferred alcohols are aliphatic monohydric alcohols containing 1 to 20 carbon atoms, particularly 1 to 6 carbon atoms, for example methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, lauryl alcohol, stearyl alcohol and the alcohols containing 6 to 13 carbon atoms obtained by the OXO process. Unsaturated alcohols such as allyl alcohol may also be used. Suitable dihydric and polyhydric alcohols include ethylene glycol and glycerol respectively. Examples of the use of alcohols are:

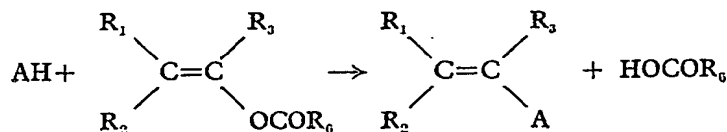
Vinyl acetate with methanol gives methyl vinyl ether

Allyl acetate with allyl alcohol gives diallyl ether

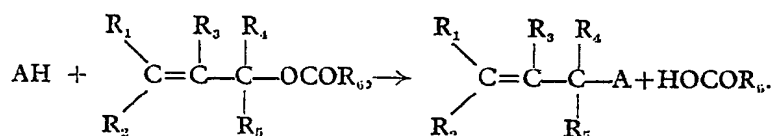
Vinyl acetate with isobutanol gives isobutyl vinyl ether.

When water is the nucleophilic reagent alcohols are obtained. In some instances the first formed alcohols are unstable and secondary products may be obtained i.e. unsubstituted vinyl esters such as vinyl acetate give acetaldehyde, the isomer or vinyl alcohol, and under conditions of low pH diallyl ether is obtained as well as allyl alcohol from allyl acetate.

In general the reaction is:



and



The process may be carried out using stoichiometric proportions of ester and nucleophilic reagent or one of the reactants may be used in excess as the solvent. Preferably however the vinyl or allyl ester is used in excess as this reduces the formation of unwanted by-products. The process may also be carried out in an inert solvent which may be an aliphatic hydrocarbon, for example pentane, hexane, octane or cyclohexane, an aromatic hydrocarbon, for example benzene, toluene or xylene, an ether, for example diethyl ether, an ester, for example dinonylphthalate, or well known solvents such as tetrahydrofuran, dioxane, dimethylacetamide, sulpholane, dimethyl sulphoxide and benzonitrile.

The process may be carried out in the temperature range $-50^{\circ}\text{C}.$ to $200^{\circ}\text{C}.$ When the nucleophilic reagent is an acid or water, preferred temperatures are in the range $50^{\circ}\text{C}.$ to $150^{\circ}\text{C}.$, but when an alcohol is used lower temperatures, i.e. $-20^{\circ}\text{C}.$ to $100^{\circ}\text{C}.$ are preferred to reduce by-product acetal formation.

The process is generally carried out at atmospheric pressure. If one of the reactants is a gas however elevated pressure may be used to increase the concentration of that reactant in the liquid phase. Alternatively if it is desired to remove a product of the process by volatilisation a reduced pressure may be employed. Suitably pressures up to 10 atmospheres may be used.

The process may be carried out in the gas as well as liquid phase. In the gas phase reaction the vinyl or allyl ester and nucleophilic reagent are passed over the Group VIII metal and copper iron, cobalt, nickel, tin or lead salt preferably supported on a support, e.g. a carbon, silica or alumina support.

It is preferable although not essential to carry out the process in the absence of oxygen which tends to initiate the polymerisation of the unsaturated reactants and/or products of the process. The reaction is preferably carried out in the presence of an inert gas, for example nitrogen or argon.

The process may be carried out in a batch-wise or continuous manner. In the liquid phase reaction it is generally advantageous to remove the unsaturated product of the reaction continuously as it is formed. This may be accomplished by means such as distillation, preferably under reduced pressure, countercurrent extraction with a solvent, or removal in a stream of inert gas. For a fully continuous process the second product of the reaction, the carboxylic acid, may also be removed continuously by taking a purge from

the reaction vessel, distilling it or extracting it continuously and thereby separating the carboxylic acid from the Group VIII metal and copper, iron, cobalt, nickel, tin or lead salt and returning the latter metal and salt to the process.

The products of the process are useful as polymerisable monomers and chemical intermediates.

The invention will now be further described with reference to the following Examples.

EXAMPLE 1

A mixture of 0.5028 gram of palladium powder, 1.5253 gram of cupric chloride and 30 mls. of allyl acetate was placed in a flask connected to a distillation column, reflux condenser and receiver. Hydrogen chloride was bubbled through the solution at 5 to 15 litres per hour. The solution was heated to the reflux temperature of allyl acetate ($103-4^{\circ}\text{C}.$). During the three hour reaction period 12 grams of allyl chloride were volatilised and collected in the receiver.

EXAMPLE 2

Example 1 was repeated using 0.5043 gram of palladium, 1.5450 grams of cupric chloride, and 70 mls. of allyl acetate. A further 40 mls. of allyl acetate were added during the reaction period. During the 2 hour reaction period 49 grams of allyl chloride were volatilised and collected in the receiver.

EXAMPLE 3

Example 1 was repeated using 0.3206 grams of palladium chloride, 1.0131 grams cupric chloride and 75 mls. of allyl acetate. A further 100 mls. of allyl acetate were added during the reaction. Hydrogen chloride was bubbled through the solution at 20 litres/hour.

During the reaction metallic palladium was precipitated and the reaction rate increased from 8.15 moles/litre/hour in the first hour to 13.1 moles/litre/hour in the second hour.

In two hours 133 grams of allyl chloride were obtained.

EXAMPLE 4

Example 3 was repeated using 0.5097 gram palladium chloride and 1.4592 grams cupric chloride. The initial solution comprised 250 mls. of a 50/50 volume per cent mixture acetic acid and allyl acetate. Hydrogen chloride was bubbled through the solution at 5 to 15 litres per hour. By addition of 340 mls. of allyl acetate during the reaction the concentration of allyl acetate was maintained at at least 35% volume per cent.

During the reaction metallic palladium was precipitated, the reaction rate increasing from 3.5 moles/litre/hour after 1 hour to a constant 4.0 moles/litre/hour. Over a period of 6 hours 250 grams of allyl chloride were obtained.

EXAMPLE 5

Example 3 was repeated using 0.5556 gram palladous chloride, 1.6852 grams ferric chloride and 150 mls. allyl acetate. The rate of hydrogen chloride addition was 10 litres/hour.

Over a period of two hours 34 grams of allyl chloride were obtained.

EXAMPLE 6

Example 1 was repeated using 0.8961 gram chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) 1.8679 gram cupric chloride and 3.05 grams stannous chloride. The solution comprised 150 mls. allyl acetate and the hydrogen chloride addition rate was 10 litres/hour.

Over a period of 4 3/4 hours 52 grams of allyl chloride were obtained.

EXAMPLE 7

Example 1 was repeated using 0.5 gram of metallic cobalt, 1.5 grams cupric chloride, 150 mls. of allyl acetate and a hydrogen chloride addition rate of 10 litres/hour.

In two hours 39 grams of allyl chloride were obtained.

EXAMPLE 8

Example 1 was repeated using 3.9815 grams of a catalyst comprising 0.5% palladium on an alumina support, 0.8988 gram cupric chloride, 150 mls. of allyl acetate and a hydrogen chloride rate of 10 litres/hour.

In 3 3/4 hours 53 grams of allyl chloride were produced.

EXAMPLE 9

A mixture of 0.982 gram of palladous chloride, 2.368 gram cupric chloride, 100 mls. of allyl acetate and 100 mls. water were placed in a flask connected to a distillation column, reflux condenser, and receiver. The solution was refluxed. Hydrogen chloride was bubbled into the solution for 20 minutes at a rate of 10 litres/hour.

After 3 hours 50 mls. of product had distilled off, of composition:

	by weight
allyl acetate	15.2%
allyl chloride	41.9%
allyl alcohol	5.2%
diallyl ether	34.4%
acrolein	2.9%

EXAMPLE 10

Example 1 was repeated using a metallic palladium concentration of 0.004 gram atoms

per litre and a varying copper chloride concentration. The following results were obtained indicating the improvement to the process of using a ratio of Group VIII metal molar concentration to copper, iron, cobalt, nickel, tin or lead salt molar concentration of at least 6:1.

CuCl_2/Pd molar ratio	Yield of allyl chloride (moles/ litre/hour)
1:1	0.2
2:1	0.5
4:1	1.0
5:1	1.3
6:1 and higher	1.7

EXAMPLE 11

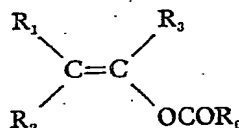
A mixture of 67.44 grams allyl acetate (0.674 mole) 0.6872 grams palladous chloride (0.0039 mole) 2.310 grams cupric chloride (0.0136 mole) and 75 grams water (4.16 mole) were heated in a flask fitted with distillation column to a temperature of 90°C. to 97°C. After 90 minutes the concentration of allyl alcohol in the solution was found to be 5% by weight (7.5 grams=0.13 mole).

EXAMPLE 12

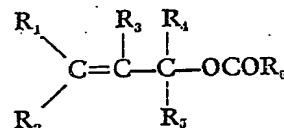
A mixture of 67.44 grams allyl acetate (0.674 mole) 1.9916 gram palladous chloride (0.0113 mole) and 5.1485 grams cupric chloride (0.0303 mole) was refluxed. A mixture of n-hexane and water was continuously run into the solution and distillate collected at the same rate. After 14 hours 420 mls. of distillate had been collected which contained 9.2% by weight allyl alcohol (38.6 grams). This represents 98% of the amount theoretically available from the amount of allyl acetate present.

WHAT WE CLAIM IS:—

1. A process for the production of olefinic compounds which comprises contacting a vinyl or allyl ester of formula



or



respectively in which R_1 , R_2 , R_3 , R_4 , R_5 are hydrogen, an organic substituent or a halogen atom and R_6 is an alkyl group with a straight or branched carbon atom chain, a substituted alkyl group, a phenyl or substituted phenyl

- group or hydrogen, with a nucleophilic reagent of formula HA in which H is hydrogen and A a nucleophilic element or group, in the presence of a Group VIII metal and a salt of copper, iron, cobalt, nickel, tin or lead.
- 5 2. A process as claimed in Claim 1 in which the Group VIII metal is palladium.
3. A process as claimed in Claim 1 or Claim 2 in which the concentration of the Group VIII metal is at least 0.00001 gram atoms per litre of solution.
- 10 4. A process as claimed in any one of the preceding claims in which the salt of copper, iron, cobalt, nickel, tin or lead is a halide or carboxylate.
- 15 5. A process as claimed in any one of the preceding claims in which the concentration of the salt of copper, iron, cobalt, nickel, tin or lead is at least 0.005 mole/litre.
- 20 6. A process as claimed in any one of the preceding claims in which the molar concentration of the salt of copper, iron, cobalt, nickel, tin or lead is at least six times the molar concentration of the Group VIII metal.
- 25 7. A process as claimed in any one of the preceding claims in which the vinyl or allyl ester is vinyl acetate, isopropenyl acetate, allyl acetate or methallyl acetate.
- 30 8. A process as claimed in any one of the preceding claims in which the nucleophilic reagent is a primary or secondary amine, a diamine, a polyamine, a phenol, a mercaptan, a thiophenol, an amide or hydrogen cyanide.
- 35 9. A process as claimed in any one of Claims 1 to 7 in which the nucleophilic reagent is an acid, alcohol or water.
10. A process as claimed in Claim 9 in which the acid is a mineral acid.
11. A process as claimed in Claim 10 in which the mineral acid is hydrochloric or hydrobromic acid.
- 40 12. A process as claimed in Claim 9 in which the acid is an aliphatic monor or dicarboxylic acid containing 1 to 20 carbon atoms or is an aromatic mono- or di-carboxylic acid.
- 45 13. A process as claimed in Claim 9 in which the alcohol is an aliphatic monohydric alcohol containing 1 to 6 carbon atoms, ethylene glycol or glycerol.
- 50 14. A process as claimed in any one of the preceding claims in which an inert solvent is present.
15. A process as claimed in any one of the preceding claims in which the temperature is in the range -50°C. to 200°C.
- 55 16. A process as claimed in any one of the preceding claims in which the pressure is up to 10 atmospheres.
17. A process as claimed in any one of the preceding claims when carried out in the gas phase, the Group VIII metal and salt of copper, iron, cobalt, nickel, tin or lead being supported on a support.
- 60 18. A process as claimed in Claim 17 in which the support is carbon, silica or alumina.
- 65 19. A process for the production of olefinic compounds substantially as described in any one of Examples 1 to 9.
20. A process for the production of olefinic compounds substantially as described in any one of Examples 10 to 12.
- 70 21. Olefinic compounds whenever produced by a process as claimed in any one of the preceding claims.
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Agent for the Applicants.

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